

PATENT SPECIFICATION

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(54) A PROCESS FOR PRODUCING AN ADHERENT METAL COATING ON AN ARTICLE

(71) We, REDERIAKTIEBOLAGET NORDSTJERNAN, a Swedish joint-stock Company of Fack, 103 80 Stockholm 7, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for producing adherent metal coatings on articles of aluminum, magnesium or alloys based on aluminium or magnesium and, in particular, to a process of pickling said articles preparatory to applying an adherent metal coating thereon.

20 Aluminum coated with an electrically conductive metal, such as copper or nickel, may be employed as an electrical conductor, for example, in home installations, or in electrical equipment, such as motors, transformers and switchboards. The purpose of such metal coatings is to reduce the contact resistance of aluminum due to the presence of a natural 25 aluminum oxide coating (Al_2O_3) which forms fairly rapidly when aluminum is exposed to the atmosphere. It is known to coat aluminum with an electro-deposited metal plate of chromium, nickel, copper, brass or silver, for decorative purposes or to provide resistance 30 to corrosion. However, a problem with such coatings is their adherence.

35 A known process for preparing an aluminum substrate is the so-called zincate process wherein the aluminum article is simultaneously pickled of its natural oxide coating and chemically coated with a layer of zinc by dipping the article in a strongly alkaline 40 zincate solution, following which the zinc-coated aluminum article is electroplated with the desired metal from an electroplating bath of the metal, e.g., baths containing nickel, copper, silver or chromium.

45 However, the zincate process has several disadvantages. For one thing, the process generally requires several inconvenient and sensitive stages of pickling and zinc-coating steps. For example, it is preferred that the zincate pickl-

ing step be repeated twice with an intermediate pickling step to remove the zinc layer formed during the first zincate pickling step so that the metal plating thereafter deposited by electrolysis will adhere to the substrate.

In bending aluminum wire pretreated according to the zincate process followed by an electroplated layer of nickel, it has been observed that cracks form in the nickel layer and that the layer tends to flake off.

Another method is known for pretreating and pickling aluminum, magnesium or alloys based on aluminium or magnesium in a mixture of hydrofluoric acid and another inorganic acid, for example, hydrochloric acid or sulphuric acid. This process is disclosed in a publication by H. W. Dettner and J. Elze entitled *Handbuch der Galvanotechnik* 1:2 (1964) published by Carl Hanser Verlag, Munchen, and also in *Aluminium-Taschenbuch* (12th edition) published by Aluminium Verlag, GmbH, Dusseldorf (1963).

A disadvantage of the foregoing methods is that the oxide layer removed in pickling immediately forms again on the metal substrate when the articles are taken out of pickling baths and exposed to air. Oxidation of the foregoing metals also occurs when the articles are washed in water after pickling in order to remove adhering films of the pickling solution. The oxide layer formed prevents or inhibits metallic contact between the metal substrate and the metal deposited on the surface which generally results in poor adhesion of the coating metal to the substrate.

The purpose of the zincate process is to avoid oxidation of pickled and oxide-free light metal surfaces by immediately forming a zinc coating after pickling is completed. However, as stated above, a disadvantage of this process is that a nickel layer applied thereto by electroplating tends to crack and flake.

Pretreatment of aluminum in an acid solution containing a dissolved metal salt prior to applying a metal coating by electrolytic or chemical plating is disclosed in a number of articles and patent specifications, among

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- which are included H. W. Dettner and J. Elze, *Handbuch der Galvanotechnik* 1:2 (1964), page 1039 (Carl Hanser Verlag, Munchen); S. Heiman, *Met. Finish* 47:9 (1949), pp. 52-56; S. Heiman, *Trans. Electrochem. Soc.* 95 (1949); pages 205-225; and U.S. Patents No. 2,580,773, No. 2,850,441, No. 2,970,090 and No. 3,672,964. All these publications disclose processes in which aluminum is pretreated in pickling baths containing hydrochloric acid and a dissolved metal salt or containing hydrofluoric acid and a dissolved metal salt.
- A process for the pretreatment of aluminum in a pickling bath of nitric acid and nickel chloride is described by G. S. Petit, R. R. W. Wright, C. C. Wright and T. Kwasnoski in *Plating* 59, 1972, pp. 567-570. In this process, the nickel layer deposited on the aluminum in pickling is removed in a following pickling process, after which the aluminum is surface coated.
- In Swedish Patent No. 108,545, a process is disclosed for making the surface of aluminum alloys rough, the surface being then pretreated in a solution containing nickel chloride, hydrogen fluoride and boric acid. In this pretreatment, a nickel layer is deposited on the aluminum surface. However, according to this patent, the nickel layer is removed before the application of a surface coating by dissolution in a mixture of nitric acid and sulphuric acid.
- It is thus apparent from the prior art referred to herein that it is known to pretreat light metals in hydrofluoric acid containing dissolved metal salts in such a way that a thin metal layer or pre-coat is deposited on the light metal in the treatment, except that the thin metal layer is thereafter removed before applying the final coating. Furthermore, it is known to surface coat light metal articles pretreated according to this technique wherein, following removal of the pre-coat, nickel or copper is directly applied using conventional techniques. However, the adhesive or bonding property of surface layers obtained in this manner is not satisfactory for many metal substrates for the reason that the metal coating tends to flake off when small mechanical loads are applied or when the substrate is deformed. In general, known processes for acid pretreatment have had their difficulties as stated above, particularly with respect to the bondability of the metal layers deposited chemically or electrolytically following pretreatment.
- A process has now been discovered for overcoming the foregoing problems wherein it has unexpectedly been found that adherent metal layers can be deposited on substrates of aluminum, magnesium and alloys based on aluminium or magnesium by employing a pretreatment step according to the invention.
- It is thus the object of the invention to provide a process for producing an adherent metal coating on substrates of aluminum, magnesium and alloys based on aluminium or magnesium.
- Another object is to provide an improved process for pretreating the surface of articles made of aluminum, magnesium and alloys based on at least one of said metals wherein the surface after pretreatment can be coated in the conventional manner with adherent metal coatings.
- These and other objects will more clearly appear when taken in conjunction with the following disclosure and the appended claims.
- According to the invention there is provided a process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium which comprises, treating the article in a solution containing at least two different inorganic acids, at least one of which is hydrofluoric acid, hydrobromic acid or hydroiodic acid, and the other of which is hydrofluoric acid, hydrobromic acid, hydroiodic acid, hydrochloric acid, phosphoric acid, chromic acid, perchloric acid or sulphuric acid, and a soluble metal salt, and then subsequently applying an adherent metal coating to the surface of the thus treated article.
- The metal salt dissolved in the pickling acid is preferably selected from the group consisting of soluble salts of nickel, chromium, iron, cobalt, manganese, magnesium or zinc. Preferably, the pH of the acid solution is below 2.5.
- The final metal coating is applied by using conventional methods in the art, for example, by electrolysis or by chemical coating. The term chemical coating is used herein to mean a process of metal coating wherein the coating is produced by chemical reaction at the surface of a substrate, for example by electroless plating or chemical vapour deposition.
- In pickling the articles of aluminium or magnesium or alloys thereof in the solutions provided by the invention, the oxide layer loosens and is removed following which the dissolved metal salt reacts with the substrate or the article and activates it for subsequent plating, such as by chemically depositing a thin layer of metal derived from the dissolved metal salt on the surface of the article. The depositing of the thin metal layer is advantageous in that it protects the substrate against oxidation when the article is removed from the solution.
- The preferred embodiments of the invention will be apparent from the following description.
- The pickling according to the invention is preferably carried out in a solution maintained at room temperature. The evaporation of the constituents in the solution is thereby

reduced which is advantageous for environmental reasons. The time of treatment in the solution is generally very short and often is less than one minute in order to assure optimum results in the final surface coating step. The time of treatment is substantially dependent on the temperature of the solution, an increase of the temperature markedly reducing the time required for treatment.

10 Suitable solutions and conditions for the treatment of aluminum and magnesium articles according to the present invention will clearly appear from the following:

15	I	Hydrochloric acid, HCl 37%	14% by weight
		Hydrofluoric acid, HF 48%	3% by weight
		Nickel chloride NiCl ₂ .6H ₂ O	10% by weight
		Water	73% by weight
20	Temperature		25°C
	Time		about 45 seconds
	Agitation		
	II	Hydrochloric acid, HCl 37%	25% by weight
25		Hydrofluoric acid, HF 48%	4% by weight
		Chromium chloride, CrCl ₃ .6H ₂ O	30% by weight
		Water	41% by weight
	Temperature		25°C
30	Time		about 50 seconds
	Agitation		
35	III	Orthophosphoric acid, H ₃ PO ₄ 85%	10% by weight
		Hydrofluoric acid, HF 48%	3% by weight
		Nickel chloride, NiCl ₂ .6H ₂ O	20% by weight
	Water		67% by weight
40	Temperature		25°C
	Time		about 35 seconds
	Agitation		

45 The adhesion between the final surface layer or metal coating and the substrate metal may be further improved by subjecting the coated substrate to a heat treatment at a temperature in excess of about 200°C, but below the melting point of the substrate metal.

50 As illustrative of the results obtained working within and outside the invention, the following examples are given.

Example 1

55 Test specimens of aluminium or magnesium were degreased and pretreated in a number of solutions of different acids. After the pretreatment, they were surface coated in conventional manner in a nickel salt solution (Watts bath) to provide nickel layers having a thickness of about 5 microns. The

adhesiveness or bonding of the nickel layer to the substrate was determined in bending tests. The surface coated and bent specimens were studied in a stereomicroscope and were evaluated into four groups divided as follows:

- | | |
|--|----|
| 1=Good quality coating substantially free from defects | 65 |
| 2=Little crack formation and flaking | |
| 3=Heavy crack formation and flaking | 70 |
| 4=Very heavy crack formation and flaking | |

For each combination of pickling baths, a group of specimens was studied, while varying the time of treatment, the temperature of the pickling bath and the composition thereof. The results of the bending test are shown in Table 1 below.

TABLE 1
Pickling Composition (in addition to
Bath water according to known
No. Techniques Evaluation

1	HCl+HF	2
2	HCl+H ₃ PO ₄	2
3	H ₃ PO ₄ +HF	4
4	HNO ₃ +HF	4
5	HNO ₃ +NiCl ₂ .6H ₂ O	4
6	HCl+MnSO ₄ .H ₂ O	4
7	HCl+NiCl ₂ .6H ₂ O	3
8	FeCl ₃ .6H ₂ O+HF	4
9	ZnSO ₄ .7H ₂ O+HF	4
10	HCl+FeCl ₃ .6H ₂ O	90

11	According to the Invention	
12	HCl+NiCl ₂ .6H ₂ O+HF	1
13	H ₃ PO ₄ +NiCl ₂ .6H ₂ O+HF	1
14	H ₂ SO ₄ +MnCl ₂ .4H ₂ O+HF	1
15	HClO ₄ +NiCl ₂ .6H ₂ O+HF	1
16	Cr ₂ O ₃ +NiCl ₂ .6H ₂ O+HF	1
17	Cr ₃ +ZnCl ₂ +HF	1
18	HCl+FeCl ₃ .6H ₂ O+HF	1
19	HCl+HBr+NiCl ₂ .6H ₂ O+HF	1
20	HCl+NiCl ₂ .6H ₂ O+HBr	2
21	HCl+NiCl ₂ .6H ₂ O+HI	2
22	HI+NiCl ₂ .6H ₂ O+HF	2

	Outside the invention and outside known techniques	105
23	HCl+CrCl ₃ .6H ₂ O	4
24	HF+NiCl ₂ .6H ₂ O	3
25	HCl+NiCl ₂ .6H ₂ O+H ₃ PO ₄	4
26	HCl+MnSO ₄ .H ₂ O+H ₂ SO ₄	3
27	HNO ₃ +AgCl	4
28	CH ₃ COOH+MnSO ₄ .H ₂ O+HF	4
29	H ₃ BO ₃ +NiF ₂ +HF	3

It has been established from the comprehensive tests enumerated in Table 1 that the best bonding or adhesion is obtained when the pickling solution, in addition to the active acid, contains one of the other acids from

- the group consisting of hydrochloric acid, hydrofluoric acid, hydrobromic acid, hydroiodic acid, phosphoric acid, chromic acid, perchloric acid and sulfuric acid (note pickling baths Nos. 11 to 19 all of which had an evaluation rating of 1). Note No. 12 which illustrates the efficacy of the HBr—HF acid system. A number of tests with other inorganic acids, such as sulphurous acid, para- and metaphosphoric acid have also shown remarkable improvement with respect to the adhesive or bonding ability but the aforementioned acids gave better and more consistent results.
- 10 Insofar as organic acids (acetic acid) have been tested to date, they have not shown positive results (pickling bath 28). The tests show that the best results with respect to the adhesive ability are achieved with hydrofluoric acid (in addition to the metal salt and the preferred inorganic acid). Hydrobromic acid and hydroiodic acid have, however, provided remarkable better results than prior art when used in place of hydrofluoric acid in the present pickling bath (pickling baths 20 and 21). However, these hydrohalic acids are more expensive and do not give the same consistently good results as hydrofluoric acid.
- 15 While the foregoing results are based on the treatment of aluminum and magnesium articles, tests have indicated that the invention can be advantageously applied to aluminum-base and magnesium-base alloys, such as the alloys referred to by the following designations: Aluminum-base alloys No. 1100, No. 3003, No. 3004, No. 5050, No. 6061, including certain castable aluminum alloys, and magnesium-base alloys No. AZ63A, No. AM100A, No. M1A, No. A3A, No. AZ61A, No. AZ80A, No. ZK60A. The best results are obtained with substantially copper-free aluminum alloys.
- 20 Similar results were obtained with respect to coating substantially pure aluminum wire containing at least 99.5% aluminum as will be apparent from the following example.
- 25 Example 2
- 30 A wire of pure aluminum (minimum 99.5% Al) was pickled according to the invention and then surface coated with 20 microns chromium by electrolysis (hard chrome plating). Treating baths and conditions appear from the following.
- 35 1. Degreasing in trichloroethylene
- 40 2. Washing to remove trichloroethylene
- 45 3. Pretreatment according to the invention
- 50 Hydrochloric acid, HCl of 37% 14% by weight

Hydrofluoric acid, HF of 48%	3% by weight	65
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10% by weight	
Water	73% by weight	
Temperature	25°C	
Time	about 45 seconds	
Agitation		70
4. Washing in water		
5. Electrolytic chromium plating in a conventional chromium bath.		
Chromium oxide, CrO_3	250 g/l	75
Sulphuric acid, H_2SO_4	2.5 g/l	
Temperature	50°C	
Current density	50 A/dm ²	
Agitation		
6. Washing in water		80
The chromium layer obtained was of even thickness and had very good adhesion to the substrate.		
Stating it broadly, the surface coating or plating of the pretreated articles is carried out using conventional processes, such as by means of known galvanotechnical methods (electroplating), by molten-metal spraying techniques, or other techniques of metal coating, such as vacuum coating methods.		85
Examples of electrolytic and chemical coating baths which may be employed for producing a substantially continuous final metal coating on aluminum and magnesium articles are as follows:		90
Sulphamate Solution		95
Nickel sulphamate, $\text{Ni}(\text{NH}_3\text{SO}_3)_2$	300 g/l	
Nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30 g/l	
Boric acid, H_3BO_3	30 g/l	
pH 3.5—4.5		100
Temperature 25 to 70°C.		
Cathodic current density 2—14 A/dm ²		
Electroless nickel coating		
Nickel chloride	30 g/l	105
Sodium hypophosphate	10 g/l	
Ammonium citrate	65 g/l	
Ammonium chloride	50 g/l	
pH 8—10		
Temperature	80—90°C	
The foregoing electroless nickel coating bath is similar to the well known process referred to in the trade as the "Kanigen" (Registered Trade Mark) process for chemically coating nickel on metal substrates.		110
Electroless cobalt coating		115
Cobalt chloride	30 g/l	
Sodium hypophosphate	20 g/l	
Sodium citrate	35 g/l	
Ammonium chloride	50 g/l	
pH 9—10		120

	Layers of coating metals such as nickel, zinc or copper, deposited according to conventional metal coating techniques on articles of aluminium or magnesium or alloys based on aluminium or magnesium, pretreated according to the present invention, can be subjected to a considerable mechanical stress without the metal layer breaking or flaking. Layers of chromium, nickel or copper deposited following the pickling process of the invention exhibit a very high brightness and are decorative. Non-coated aluminium articles always have a dull appearance due to the presence of a surface layer of aluminum oxide.	H ₃ PO ₄ ; Chromic acid (Cr ₂ O ₇); HClO ₄ and H ₂ SO ₄	0.5% to 20%	55
5	(3) Soluble metal salt	(3)	0.5% to 50%	
10	(4) Water	(4)	essentially the balance	
WHAT WE CLAIM IS:—				60
15	1. A process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium which comprises, treating the article in a solution containing at least two different inorganic acids, at least one of which is hydrofluoric acid, hydrobromic acid or hydroiodic acid, and the other of which is hydrofluoric acid, hydrobromic acid, hydroiodic acid, hydrochloric acid, phosphoric acid, chromic acid, perchloric acid or sulfuric acid, and a soluble metal salt, and then subsequently applying an adherent metal coating to the surface of the thus treated article.	1. A process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium which comprises, treating the article in a solution containing at least two different inorganic acids, at least one of which is hydrofluoric acid, hydrobromic acid or hydroiodic acid, and the other of which is hydrofluoric acid, hydrobromic acid, hydroiodic acid, hydrochloric acid, phosphoric acid, chromic acid, perchloric acid or sulfuric acid, and a soluble metal salt, and then subsequently applying an adherent metal coating to the surface of the thus treated article.	1. A process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium which comprises, treating the article in a solution containing at least two different inorganic acids, at least one of which is hydrofluoric acid, hydrobromic acid or hydroiodic acid, and the other of which is hydrofluoric acid, hydrobromic acid, hydroiodic acid, hydrochloric acid, phosphoric acid, chromic acid, perchloric acid or sulfuric acid, and a soluble metal salt, and then subsequently applying an adherent metal coating to the surface of the thus treated article.	65
20	2. A process according to claim 1 wherein the metal salt is a soluble salt of a metal having the same position as or below magnesium in the electromotive series.	2. A process according to claim 1 wherein the metal salt is a soluble salt of a metal having the same position as or below magnesium in the electromotive series.	2. A process according to claim 1 wherein the metal salt is a soluble salt of a metal having the same position as or below magnesium in the electromotive series.	70
25	3. A process according to claim 2, wherein the metal salt is a soluble salt of nickel, chromium, iron, cobalt, manganese, magnesium or zinc.	3. A process according to claim 2, wherein the metal salt is a soluble salt of nickel, chromium, iron, cobalt, manganese, magnesium or zinc.	3. A process according to claim 2, wherein the metal salt is a soluble salt of nickel, chromium, iron, cobalt, manganese, magnesium or zinc.	75
30	4. A process according to any one of claims 1 to 3 wherein the metal coating is applied by electrolysis or by chemical coating (as hereinbefore defined).	4. A process according to any one of claims 1 to 3 wherein the metal coating is applied by electrolysis or by chemical coating (as hereinbefore defined).	4. A process according to any one of claims 1 to 3 wherein the metal coating is applied by electrolysis or by chemical coating (as hereinbefore defined).	80
35	5. A process according to any one of claims 1 to 4 wherein the pH of the solution is less than 2.5.	5. A process according to any one of claims 1 to 4 wherein the pH of the solution is less than 2.5.	5. A process according to any one of claims 1 to 4 wherein the pH of the solution is less than 2.5.	85
40	6. A process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.	6. A process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.	6. A process for producing an adherent metal coating on an article of aluminium, magnesium or an alloy based on aluminium or magnesium according to claim 1 substantially as hereinbefore described with reference to any one of the Examples.	90
45	5. An article of aluminium, magnesium or an alloy based on aluminium or magnesium having an adherent metal coating thereon applied by a process according to any one of the preceding claims.	5. An article of aluminium, magnesium or an alloy based on aluminium or magnesium having an adherent metal coating thereon applied by a process according to any one of the preceding claims.	5. An article of aluminium, magnesium or an alloy based on aluminium or magnesium having an adherent metal coating thereon applied by a process according to any one of the preceding claims.	95
	Boardly, the solution composition may range by weight as follows:			100
50	(1) Active acid from the group consisting of HF, HBr and HI 0.1% to 10%	(1) Active acid from the group consisting of HF, HBr and HI 0.1% to 10%	For the Applicants, CARPMAELS & RANSFORD, Chartered Patent Agents, 43 Bloomsbury Square, London, WC1A 2RA.	
	(2) Other inorganic acids HCl, HF; HBr; HI;	(2) Other inorganic acids HCl, HF; HBr; HI;		

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